

CLAIMS

I Claim:

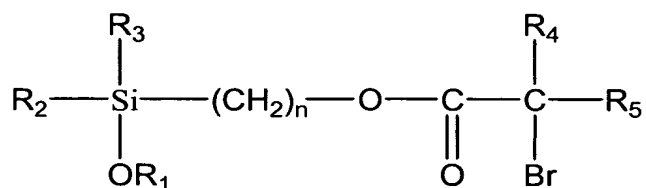
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1. A process for growing a polyethylene glycol alkyl acrylate polymer film gradient on a substrate having a moiety accepting surface comprising:

(a) contacting at least one initiator molecule with the moiety accepting surface of a substrate to form an initiator coated substrate, said initiator molecule comprising at least one of

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i)



wherein:

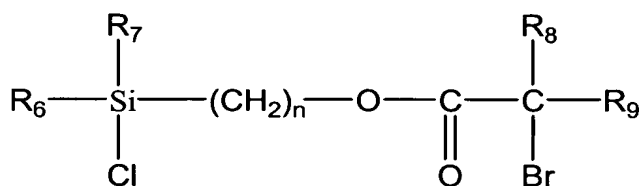
n is an integer of 1 to 50;

R<sub>1</sub> and R<sub>4</sub> are each independently a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons;

15

R<sub>2</sub> and R<sub>3</sub> are each independently a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, OR<sub>1</sub>, or an alkyl of 3 to 20 carbons; and

R<sub>5</sub> is a H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons,



20

ii)

wherein:

n is an integer of 1 to 50;

R<sub>6</sub> and R<sub>7</sub> are each independently Cl, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons;

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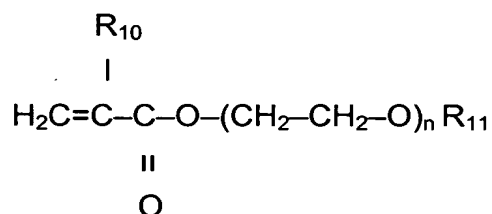
R<sub>8</sub> is a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons; and

R<sub>9</sub> is a H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons, and

- iv) mixtures thereof;
- (b) adding a first and second layer of liquid to a coating container, said first and second layer of liquid being added as separate discrete additions to said container;

wherein said first liquid layer comprises polyethylene glycol alkyl acrylate monomers in solution and said second liquid layer comprises a liquid having a different polyethylene glycol alkyl acrylate monomer concentration than said first liquid layer;

wherein said polyethylene glycol alkyl acrylate monomer has the general formula



wherein:

n is an integer of 1 to 100; and

R<sub>10</sub> and R<sub>11</sub> are each independently H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 1 to 20 carbons; and

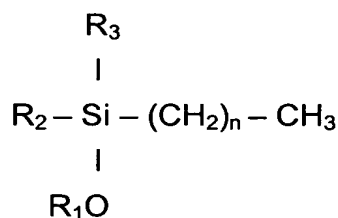
wherein at least one catalyst and optionally at least one ligand are added to the solution containing the polyethylene glycol alkyl acrylate monomer;

- (c) inserting the initiator-coated substrate of step (a) into the coating container; and

- (d) allowing a sufficient amount of time for diffusion of the polyethylene glycol alkyl acrylate monomer to occur between said first and second liquid layers, wherein a polyethylene glycol alkyl acrylate gradient is grown on the surface of the initiator-coated substrate.

2. The process according to claim 1, wherein the moiety accepting surface of the substrate is further contacted in step (a) with at least one spacer molecule, wherein said spacer molecule comprises at least one of

- (i) alkyl chains having the following general formulas

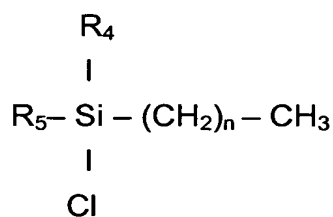


wherein:

n is an integer of 1 to 50;

R<sub>1</sub> is a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons;

R<sub>2</sub> and R<sub>3</sub> are each independently a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, OR<sub>1</sub>, or an alkyl of 3 to 20 carbons; and

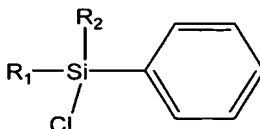


wherein:

n is an integer of 1 to 50;

R<sub>4</sub> and R<sub>5</sub> are each independently Cl, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons;

(ii) phenyl and phenyl derivatives having the following general formula

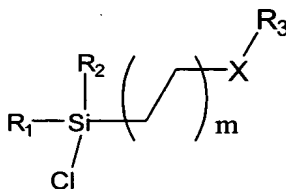


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wherein:

R<sub>1</sub> and R<sub>2</sub> are each independently Cl, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons; and

10 (iii) a mixture of alkyl chains and functional groups having the following general formula



wherein:

m is an integer of 1 to 50;

15 R<sub>1</sub> and R<sub>2</sub> are each independently Cl, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons;

R<sub>3</sub> is a phenyl, OH, NH<sub>2</sub>, or an alkyl of 3 to 20 carbons; and

X is an O, COO, or a CONH.

20 3. The process according to claim 2, wherein the spacer molecule is n-propyl triethoxysilane.

4. The process according to claim 2, wherein the initiator to spacer molecule ratio ranges from about 1:99 to about 99:1.

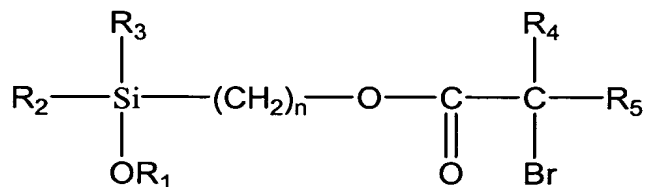
25 5. The process according to claim 1 or 2, wherein the initiator molecule is 5'-(triethoxysilylpentyl) 2-bromo-2-methylpropionate.

6. The process according to claim 1 or 2, wherein the polyethylene glycol alkyl acrylate monomer is polyethylene glycol methacrylate.

7. The process according to claim 1 or 2, wherein the substrate is selected from the group consisting of glass, metal oxide, silicon, fabric, quartz, zirconia and polymeric resins.
- 5
8. The process according to claim 1 or 2, wherein the polyethylene glycol alkyl acrylate film gradient grown on the surface of the substrate has a thickness ranging from about 0.5 nm to about 5000 nm.
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9. The process according to claim 1 or 2, wherein the polyethylene glycol alkyl acrylate film gradient grown on the surface of the substrate has a polyethylene glycol alkyl acrylate chain density ranging from about 0.5% to about 100%.
- 15
10. The process according to claim 1 or 2, wherein the second liquid layer is water.
11. The process according to claim 1 or 2, wherein the second liquid layer is selected from the group consisting of a polyethylene glycol alkyl acrylate monomer solution having a lower concentration of
- 20
- polyethylene glycol alkyl acrylate monomers than the first liquid layer, a polyethylene glycol alkyl acrylate monomer solution having a higher concentration of polyethylene glycol alkyl acrylate monomers than the first liquid layer, an organic solvent, and a polar solvent.
- 25
12. The process according to claim 11, wherein said polar solvent is water.
13. The process according to claim 1 or 2, further comprising baking the substrate after said substrate is coated with the at least one initiator molecule in step (a), wherein said substrate is baked in an oven at a
- 30
- temperature ranging from 100° C to 180° C for a time period ranging from 30 minutes to 10 hours.
14. The process according to claim 1 or 2, wherein the first liquid layer of step (b) further comprises a polar solvent.
- 35
15. The process according to claim 14, wherein the polar solvent is water.

16. The process according to claim 1 or 2, wherein step (a) is performed in the presence of a solvent.
- 5 17. The process according to claim 16, wherein said solvent is selected from the group consisting of water, hydrocarbons, ethers, halogenated hydrocarbons, ketones, methyl ethyl ketones, methyl isobutyl ketones, alcohols, nitriles, esters, carbonates, inorganic solvents, and mixtures thereof.
- 10 18. The process according to claim 1 or 2, wherein the ligand is selected from the group consisting of 2,2'-bipyridyl, 1,10-phenanthroline, an alkylamine, a polyamine, and a trialkoxyaluminum.
- 15 19. The process according to claim 1 or 2, wherein the catalyst is selected from the group consisting of cuprous chloride, cupric chloride, cuprous bromide, cuprous iodide, cuprous cyanide, cuprous oxide, cuprous acetate, cuprous perchlorate, a tris(phenylphosphine) complex of divalent ruthenium ( $\text{RuCl}_2(\text{PPh}_3)_3$ ), and tris(phenylphosphine) complex of divalent iron ( $\text{FeCl}_2(\text{PPh}_3)_3$ ).
- 20 20. A substrate having deposited thereon a polyethylene glycol alkyl acrylate polymer film gradient comprising
- 25 (a) at least one initiator molecule selected from the group consisting of

i)

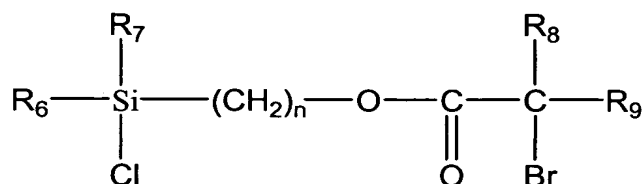


- 30 wherein:  
n is an integer of 1 to 50;

R<sub>1</sub> and R<sub>4</sub> are each independently a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons;

R<sub>2</sub> and R<sub>3</sub> are each independently a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, OR<sub>1</sub>, or an alkyl of 3 to 20 carbons; and

5 R<sub>5</sub> is a H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons,



ii)

wherein:

10 n is an integer of 1 to 50;

R<sub>6</sub> and R<sub>7</sub> are each independently Cl, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons;

R<sub>8</sub> is a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons; and

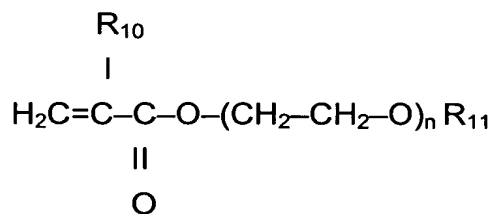
R<sub>9</sub> is a H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons, and

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iii) mixtures thereof; and

(b) at least one polyethylene glycol alkyl acrylate monomer having the general formula

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wherein:

n is an integer of 1 to 100; and

R<sub>10</sub> and R<sub>11</sub> are each independently H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 1 to 20 carbons.

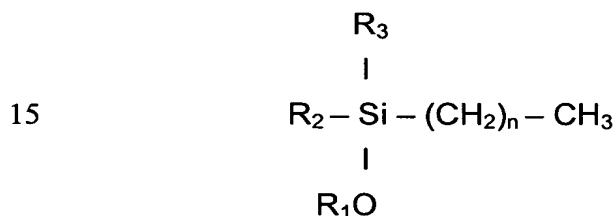
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21. The substrate of claim 20, wherein the initiator molecule of the polymer film gradient is 5'-(triethoxysilylpentyl) 2-bromo-2-methylpropionate.

5 22. The substrate of claim 20, wherein the polyethylene glycol alkyl acrylate monomer of the polymer film gradient is polyethylene glycol methacrylate.

10 23. The substrate according to claim 20, wherein the polymer film gradient further comprises a spacer molecule comprising at least one of

(i) alkyl chains having the following general formulas

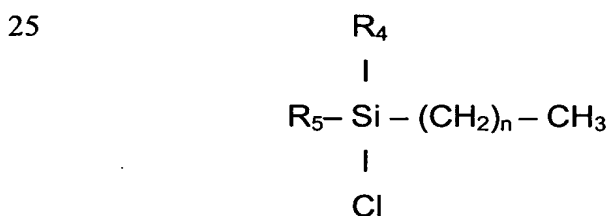


wherein:

20 n is an integer of 1 to 50;

R<sub>1</sub> is a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons;

R<sub>2</sub> and R<sub>3</sub> are each independently a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, OR<sub>1</sub>, or an alkyl of 3 to 20 carbons; and



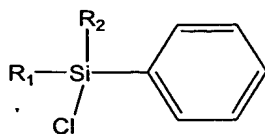
wherein:

n is an integer of 1 to 50;

R<sub>4</sub> and R<sub>5</sub> are each independently Cl, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons;

35 (ii) phenyl and phenyl derivatives having the following general formula



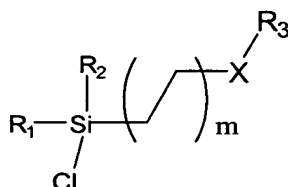


wherein:

$R_1$  and  $R_2$  are each independently Cl,  $CH_3$ ,  $C_2H_5$ , or an alkyl of 3 to 20 carbons; and

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(iii) a mixture of alkyl chains and functional groups having the following general formula



wherein:

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$m$  is an integer of 1 to 50;

$R_1$  and  $R_2$  are each independently Cl,  $CH_3$ ,  $C_2H_5$ , or an alkyl of 3 to 20 carbons;

$R_3$  is a phenyl, OH,  $NH_2$ , or an alkyl of 3 to 20 carbons; and

$X$  is an O, COO, or a CONH.

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24. The substrate according to claim 23, wherein the spacer molecule of the polymer film gradient is *n*-propyl triethoxysilane.

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25. The substrate according to claim 23, wherein the polymer film gradient has an initiator to spacer molecule ratio ranging from about 1:99 to about 99:1.

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26. The substrate according to claim 20 or 23, wherein said substrate is selected from the group consisting of glass, metal oxide, silicon, fabrics, porous substrates, quartz, polymeric substrates reinforced with other inorganic materials, zirconia and polymeric resins.

27. A substrate having a moiety accepting surface coated according to the process of claim 1 or 2.

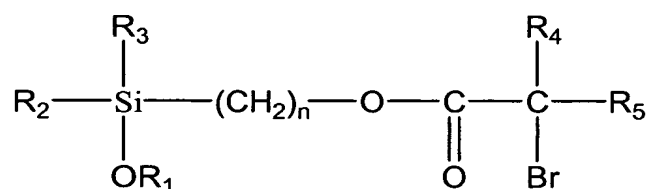
28. The substrate of 27, wherein said substrate is selected from the group consisting of glass, metal oxide, silicon, fabrics, porous substrates, quartz, polymeric substrates reinforced with other inorganic materials, zirconia and polymeric resins.
29. The substrate of claim 27, wherein the moiety accepting surface of the substrate has a polyethylene glycol alkyl acrylate chain density ranging from about 0.1% to about 100%.
30. A process for growing a polyethylene glycol methacrylate gradient film on a substrate having a hydroxylated surface comprising
- (a) contacting 5'-(triethoxysilylpentyl) 2-bromo-2-methylpropionate with the hydroxylated surface of the substrate in the presence of toluene to form an initiator-coated substrate;
  - (b) inserting said initiator-coated substrate into a container sized to accommodate the initiator-coated substrate;
  - (c) adding a first and second layer of liquid to a coating container, said first and second layer of liquid being added as separate discreet additions to said container;
- wherein said first liquid layer comprises polyethylene glycol methacrylate monomers in solution, bipyridyl, cuprous chloride, cupric chloride and water;
- wherein said second liquid layer comprises water; and
- (d) allowing a sufficient amount of time for diffusion of the polyethylene glycol methacrylate monomers to occur between said first and second liquid layers, wherein a polyethylene glycol methacrylate gradient is grown on the surface of the initiator-coated substrate.

31. The process according to claim 30, wherein the hydroxylated surface of the substrate is further contacted in step (a) with n-propyl triethoxysilane.

5 32. A process for growing a polyethylene glycol alkyl acrylate polymer film gradient on a substrate having a moiety accepting surface comprising

(a) contacting at least one initiator molecule with the moiety accepting surface of a substrate to form an initiator coated substrate, said  
10 initiator molecule comprising at least one of

i)



wherein:

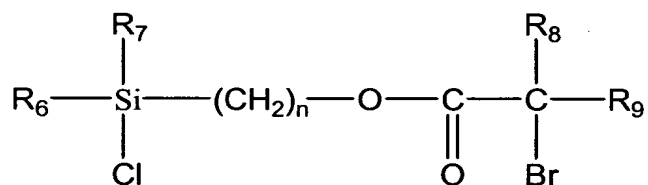
n is an integer of 1 to 50;

15  $\text{R}_1$  and  $\text{R}_4$  are each independently a  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , or an alkyl of 3 to 20 carbons;

$\text{R}_2$  and  $\text{R}_3$  are each independently a  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{OR}_1$ , or an alkyl of 3 to 20 carbons; and

$\text{R}_5$  is a H,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , or an alkyl of 3 to 20 carbons,

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ii)

wherein:

25 n is an integer of 1 to 50;

$\text{R}_6$  and  $\text{R}_7$  are each independently Cl,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , or an alkyl of 3 to 20 carbons;

R<sub>8</sub> is a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons; and  
R<sub>9</sub> is a H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons, and

iii) mixtures thereof;

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(b) adding a first and second liquid layer to two separate coating  
containers;

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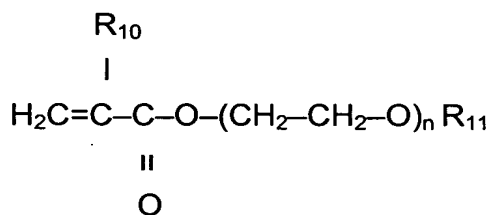
wherein the two separate coating containers are connected with a  
micro-channel;

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wherein said first liquid layer comprises polyethylene glycol alkyl  
acrylate monomers in solution and said second liquid layer  
comprises a liquid having a different polyethylene glycol alkyl  
acrylate monomer concentration than said first liquid layer;

wherein said polyethylene glycol alkyl acrylate monomer has the  
general formula

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wherein:

n is an integer of 1 to 100; and

R<sub>10</sub> and R<sub>11</sub> are each independently H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 1  
to 20 carbons; and

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wherein at least one catalyst, optionally at least one ligand, and  
optionally a polar solvent are added to the first liquid layer;

(c) inserting the initiator-coated substrate of step (a) into the micro-  
channel; and

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(d) allowing a sufficient amount of time for diffusion of the polyethylene glycol alkyl acrylate monomer to occur between said first and second liquid layers, wherein a polyethylene glycol alkyl acrylate gradient is grown on the surface of the initiator-coated substrate.

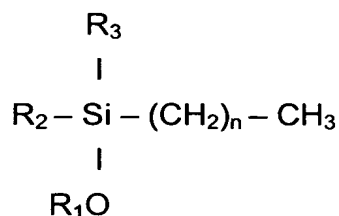
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33. The process according to claim 32, wherein the moiety accepting surface of the substrate is further contacted in step (a) with at least one spacer molecule, wherein said spacer molecule comprises at least one of

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(i) alkyl chains having the following general formulas

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wherein:

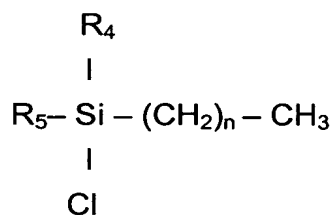
n is an integer of 1 to 50;

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R<sub>1</sub> is a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons;

R<sub>2</sub> and R<sub>3</sub> are each independently a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, OR<sub>1</sub>, or an alkyl of 3 to 20 carbons; and

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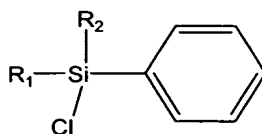
wherein:

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n is an integer of 1 to 50;

R<sub>4</sub> and R<sub>5</sub> are each independently Cl, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons;

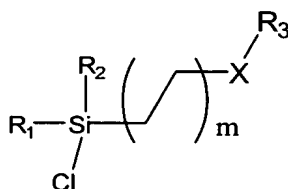
(ii) phenyl and phenyl derivatives having the following general formula



wherein:

5  $R_1$  and  $R_2$  are each independently Cl, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons; and

(iii) a mixture of alkyl chains and functional groups having the following general formula



wherein:

$m$  is an integer of 1 to 50;

$R_1$  and  $R_2$  are each independently Cl, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or an alkyl of 3 to 20 carbons;

15  $R_3$  is a phenyl, OH, NH<sub>2</sub>, or an alkyl of 3 to 20 carbons; and  
X is an O, COO, or a CONH.